

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

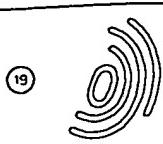
Defective images within this document are accurate representation of
The original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 467 007 A1

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: 90870113.9

(51) Int. Cl.⁵: C07C 15/02

(22)

Date of filing: 18.07.90

(43)

Date of publication of application:
22.01.92 Bulletin 92/04

(71) Applicant: FINA TECHNOLOGY, INC.
8350 North Central Expressway
Dallas, Texas 75206(US)

(84)

Designated Contracting States:
BE DE FR GB IT NL

(72) Inventor: Butler, James R.
15718 Crestbrook Drive
Houston, Texas(US)

(74) Representative: Leyder, Francis et al
c/o Fina Research S.A. Zone Industrielle C
B-6520 Feluy (Feluy)(BE)

(54) Transalkylation process.

(57) Alkylation-transalkylation process involving alkylation of an aromatic substrate with a C₂-C₄ alkylating agent coupled with separation to recover a monoalkylated aromatic product and liquid phase transalkylation of a polyalkylated product. Both the alkylation and transalkylation reactions carried out in the liquid phase over molecular sieve aromatic alkylation and transalkylation catalysts. The output from the alkylation reaction zone is separated to provide a lower boiling fraction comprising the aromatic substrate and a higher boiling fraction comprising a mixture of monoalkylated and polyalkylated aromatics which is separated to produce the monoalkylated fraction and a higher boiling polyalkylated fraction.

At least a portion of the polyalkylated fraction including substantially all dialkylated and trialkylated aromatics is supplied, along with the aromatic substrate, to a transalkylation reaction zone operated under liquid phase conditions, to cause disproportionation of the polyalkylated fraction to arrive at a disproportionation product having a reduced polyalkylated aromatic content and an enhanced monoalkylated aromatic content which is supplied to the first separation zone.

A benzene feed stock and a C₂-C₄ alkylating agent are supplied to an alkylation reaction zone containing a molecular sieve alkylation catalyst and which is operated to produce an alkylated product comprising a mixture of monoalkyl and polyalkyl benzenes. The alkylation zone may be operated under liquid phase or vapor phase conditions with the output from the alkylation zone being subjected to separation steps. The transalkylation reaction zone is operated at an average temperature below the average temperature of the alkylation reaction zone and under conditions to maintain the benzene in the liquid phase.

In the production of ethylbenzene, in which the alkylation reaction takes place over an aromatic alkylation catalyst selected from the group consisting of zeolite beta and zeolite omega, the output from the alkylation reaction zone is supplied to a benzene separation zone. A higher boiling fraction comprising an ethylbenzene/polyethylbenzene mixtures is supplied from the benzene separation zone to an ethylbenzene separation zone. This zone is operated to produce a lower boiling product fraction comprising ethylbenzene and a higher boiling fraction comprising polyethylbenzene containing no more than 5 wt. % ethylbenzene. The polyethylbenzene fraction is supplied along with benzene to a transalkylation reaction zone which preferably contains a transalkylation catalyst selected from the group consisting of zeolite y and zeolite omega.

EP 0 467 007 A1

with recycle of the transalkylated product to an intermediate separation zone. In the Barger process, the temperature and pressure conditions are adjusted so that the alkylation and transalkylation reactions take place in essentially the liquid phase. The transalkylation catalyst is an aluminosilicate molecular sieve including X-type, Y-type, ultrastable-Y, L-type, omega type and mordenite type zeolites with the latter being preferred. The catalyst employed in the alkylation reaction zone is a solid phosphoric acid containing material. Aluminosilicate alkylation catalysts may also be employed and water varying from 0.01 to 6 volume percent is supplied to the alkylation reaction zone. The output from the alkylation reaction zone is supplied to first and second separation zones. In the second reaction zone intermediate aromatic products and trialkylaromatic and heavier products are separated to provide an input to the transalkylation reaction zone having only dialkyl aromatic components, or diethylbenzene in the case of an ethylbenzene manufacturing procedure or diisopropylbenzene in the case of cumene production. A benzene substrate is also supplied to the transalkylation zone for the transalkylation reaction and the output from the transalkylation zone is recycled to the first separation zone. The alkylation and transalkylation zones may be operated in a downflow, upflow or horizontal flow configurations.

15

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided an alkylation-transalkylation process involving alkylation of an aromatic substrate with a C₂-C₄ alkylating agent coupled with separation to recover a monoalkylated aromatic product and liquid phase transalkylation of a polyalkylated product. In one aspect of the invention, both the alkylation and transalkylation reactions are carried out in the liquid phase over molecular sieve aromatic alkylation and transalkylation catalysts. The output from the alkylation reaction zone is supplied to a separation zone which is operated to produce a lower boiling fraction comprising the aromatic substrate, which may be recycled to the alkylation reaction zone, and a higher boiling fraction comprising a mixture of monoalkylated and polyalkylated aromatics. The higher boiling fraction is supplied to a second separation zone to produce a second lower boiling fraction comprising the desired monoalkylated product and a higher boiling fraction comprising polyalkylated product.

At least a portion of the polyalkylated fraction including substantially all dialkylated and trialkylated aromatics is supplied, along with the aromatic substrate, to a transalkylation reaction zone containing a molecular sieve transalkylation catalyst. The transalkylation zone is operated under liquid phase conditions to cause disproportionation of the polyalkylated fraction to arrive at a disproportionation product having a reduced polyalkylated aromatic content and an enhanced monoalkylated aromatic content. At least a portion of the disproportionation product is supplied to the first separation zone. In a specific application of the invention directed to the production of ethylbenzene or cumene, the output from the transalkylation zone is supplied to a third separation zone from which benzene and a monalkyl benzene fraction (ethylbenzene or cumene) is recovered and recycled to the separation zone.

In another embodiment of the invention, a benzene feed stock and a C₂-C₄ alkylating agent are supplied to an alkylation reaction zone containing a molecular sieve alkylation catalyst and which is operated to produce an alkylated product comprising a mixture of monoalkyl and polyalkyl benzenes. In this embodiment of the invention the alkylation zone may be operated under liquid phase or vapor phase conditions with the output from the alkylation zone being subjected to separation steps as described above. The transalkylation reaction zone is operated at an average temperature below the average temperature of the alkylation reaction zone and under conditions to maintain the benzene in the liquid phase. In a specific application of this embodiment of the invention to a procedure employing vapor phase ethylation of benzene followed by liquid phase transalkylation, the average temperature of the transalkylation reaction zone is at least 100°C less than the average temperature of the alkylation reaction zone.

In yet a further aspect of the invention involving the alkylation of a benzene feed stock with a C₂-C₄ alkylating agent, the alkylation catalyst is selected from the group consisting of zeolite beta zeolite omega, and zeolite Y and the alkylation reactor is operated under conditions to maintain the benzene feed stock in the liquid phase as described previously. The effluent from the alkylation reactor is subjected to separation steps along the lines described above and subsequent to separation to recover the desired monoalkylbenzene product, e.g., ethylbenzene or cumene, at least a portion of the polyalkylbenzene fraction including substantially all of the dialkylbenzene content and a predominant portion of the trialkylbenzene content is supplied to the transalkylation zone containing a transalkylation catalyst selected from a group consisting of a zeolite y and zeolite omega. Preferably the alkylation catalyst comprises zeolite beta. It is also preferred that the transalkylation catalyst comprise zeolite omega.

In a further embodiment of the invention directed specifically to the production of ethylbenzene, in which the alkylation reaction takes place over an aromatic alkylation catalyst selected from the group

polyethylbenzene transalkylation in a separate reactor under relatively mild liquid phase conditions, minimizes the xylene make in the manufacturing process. This enables ethylbenzene recirculation to be reduced by limiting the ethylbenzene content in the polyethylbenzene fraction to 5 wt.% or less and, where preferred catalysts are used to further minimize xylene make, down to about 2 wt.% or less ethylbenzene.

- 5 A preferred aspect of the present invention involves supplying the polyethylbenzene fraction, including both diethylbenzene and the triethylbenzene and higher molecular weight compounds to the transalkylation reactor as contrasted with separating out a substantial portion of the diethylbenzene for recycle to the alkylation zone, as disclosed in the aforementioned patent to Wight, or separating out trialkylaromatics with transalkylation only of dialkylbenzene, as disclosed in the aforementioned patent to Barger. In this respect,
- 10 depending upon the configuration of the interface of the transalkylation reactor and polyethylbenzene or other separation zones, substantially all of the diethylbenzene and substantially all or most of the triethylbenzene content will be supplied to the transalkylation reactor. In either case, the practical effect of this embodiment of the invention is that recycle to the alkylation reactor is limited to benzene and lighter components, e.g., ethylene, while most, if not all of the triethylbenzenes together with diethylbenzenes are
- 15 retained in the system ultimately for conversion to benzene and ethylbenzene. This offers significant advantages over the prior art processes, not only in terms of reduced xylene make as described previously, but also in terms of ultimate product yield.

In experimental work relative to the invention a number of catalysts were employed in transalkylation tests carried out in an upflow, flooded-bed reactor, that is, only a liquid phase was in contact with the catalyst. The feed employed in this experimental work was an approximate 1:1 mixture of benzene and the polyethylbenzene overheads fraction from a commercial operation employing vapor-phase alkylation of benzene to produce ethylbenzene. A typical feed employed in the experimental work had the composition as shown below in Table I.

25

TABLE I

	Component	Wt.%
30	Non-aromatics	0.032
	Benzene	50.241
	Toluene	0.000
	Ethylbenzene	6.117
	p + M-Xylene	0.000
35	Styrene	0.063
	o-Xylene	0.066
	Cumene	3.973
	n Propylbenzene	7.816
	m + p Ethyltoluene	2.053
40	1,3,5-Trimethylbenzene	0.128
	o-Ethyltoluene	0.356
	1,2,4-Trimethylbenzene	0.536
	1,2,3-Trimethylbenzene	0.401
	m-Diethylbenzene	14.808
45	o + p-Diethylbenzene	7.328
	Butylbenzenes	1.653
	Heavies	4.429

In the experimental work, the average pressure was about 300 psia with a pressure drop across the reactor ranging from about 5 to 15 psi. The temperature profile across the reactor was relatively constant with an endotherm from the inlet to the outlet of less than 10 °C and usually less than 5 °C. The experimental runs were initiated at relatively low temperatures, usually less than 100 °C and progressively increased as described later. The space velocity was maintained relatively constant at a value of 6 hr⁻¹ (LHSV) based on the total hydrocarbon feed. Diethylbenzene conversions and selectivity to ethylbenzene were measured as a function of catalyst age (duration of the run) along with the production of various other components including xylenes.

In a first test run, the catalyst used was a commercially available zeolite Y (identified herein as Catalyst A) in which the inlet temperature was progressively increased up to about 235 °C and stabilized there with an average temperature increase through the reactor of only 1 °C or 2 °C. The results of this experimental

Yet additional experimental work was carried out employing the zeolite Y identified above as catalyst B in which the feed was a relatively pure diethylbenzene mixed in approximately equal parts with benzene. Unlike the feed stock employed in the experiment work of FIGURES 1 through 4, the pure diethylbenzene feed stock contained only very small amounts of material susceptible to cracking or other conversion reactions, e.g., deethylation, to produce xylenes and was also free of xylenes. The make up of the feed stock in this experimental work is set forth below in Table II.

TABLE II

	Components	Wt.%
10	Non Aromatics	0.01
15	Benzene	56.58
	Toluene	0.09
20	Ethylbenzene	0.01
	Xylenes	0.0000
25	n-PR-BZ	0.02
	m,p-ethyltoluene	0.03
	o-ethyltoluene	0.01
	124 trimethylbenzene	
	sec-BU-BZ	0.47
	123 Trimethylbenzene	
	m,Diethylbenzene	27.62
	o,p-diethylbenzene	14.27
	n-BU-BZ	0.35
	Heavies	0.54

In this test run, the inlet and outlet pressures were held at 310 and 305 psig, respectively. The average temperature of the reactor was increased approximately linearly with time from an initial value of about 30 198° to a final value of about 298°C. The space velocity was generally held within the range of about 5.8-6.0hr⁻¹ (LHSV) with the exception of about two-thirds of the way through the test where it fell to about 5.1 before recovering to the higher value.

The results of this test run are set forth in FIGURES 5 and 6. In FIGURE 5a, curve 38 is a graph of temperature, T, versus catalyst age A in hours on the abscissa. In FIGURE 5b curves 40 and 41 are graphs of percent selectivity to ethylbenzene and percent ethylbenzene conversion, respectively. Curve 42 is a graph of the total xylene make, X, expressed in ppm, based upon the amount of ethylbenzene produced. FIGURE 6, shows the relationship between ethylbenzene conversion and temperature. Curve 43 is a graph of ethylbenzene conversion, C, on the ordinate versus temperature, T, on the abscissa.

As indicated by the data set forth in FIGURE 5, xylene make remained low throughout the test run. No xylene was produced until the temperature was increased to about 260°C (which generally corresponded to the reduction in space velocity to about 5.1 hours⁻¹ as reported previously). Percent conversion remained good until the temperature was increased above 280°C. As indicated in FIGURE 6, ethylbenzene conversion appears to remain above 50% over a temperature range of about 200°-290°C with the optimum range appearing to be about 210° to 280°C.

With further reference to the drawings, FIGURE 7 through 10 illustrate schematic flow diagrams illustrating different embodiments of the invention. It will be assumed for purposes of discussion that the invention is applied in the production of ethylbenzene by reaction of ethylene with benzene and that the alkylation reaction as carried out in a flooded-bed liquid-phase alkylation reactor employing zeolite beta, zeolite Y or zeolite omega as the alkylation catalyst. However, as noted previously and as discussed in greater detail below, the alkylation step can be conducted as a vapor- phase reaction employing a catalyst such as silicalite or ZSM-5.

Referring first to FIGURE 7, a feed stream 50 containing ethylene and benzene supplied via lines 51 and 52, respectively, is passed first to a dehydrator 54, where the water content is reduced to a level of about 100 ppm or less, preferably about 50 ppm or less, and then to an alkylation reaction zone 56. The alkylation reactor which may comprise a plurality of series connected adiabatic reactors with interstage injection of ethylene and also interstage cooling, normally will be operated at an average temperature of about 220°C and under sufficient pressure, about 600 psia or above, to maintain the benzene in the liquid phase and at least about 2 mole percent of ethylene solubilized in the benzene. As an alternative to using

stream by purge line 88. The overheads fraction is recycled through line 89 to the benzene column similarly as described above.

- The embodiment of FIGURE 10 is similar to that of FIGURE 9 except that the transalkylation reactor output is split, with a portion being directly supplied to the benzene column 61 via line 92 and the remainder to the separation zone 86 which is operated as described above. The configuration of FIGURE 10 provides a means for maintaining a low concentration of C₉ and C₁₀ hydrocarbons in the system and reduces the energy costs of operating column 86. Typically about 60% or more of the transalkylation reactor output is recycled directly to the benzene column 61 with the remainder being directed to the separation zone 86.
- Having described specific embodiments of the present invention, it will be understood that modification thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.

Claims

15

1. In an alkylation-transalkylation process, the steps comprising:
 - a) supplying a feed stock containing an aromatic substrate into a reaction zone containing a molecular sieve aromatic alkylation catalyst;
 - b) supplying a C₂-C₄ alkylating agent to said reaction zone;
 - c) operating said reaction zone at temperature and pressure conditions to maintain said aromatic substrate in the liquid phase and causing alkylation of said aromatic substrate by said alkylating agent in the presence of said catalyst to produce an alkylated product comprising a mixture of monoalkylated and polyalkylated aromatic products;
 - d) recovering said alkylated product from said reaction zone and supplying said product from said reaction zone to a separation zone for the separation of said aromatic substrate;
 - e) operating said separation zone to produce a lower boiling fraction comprising said aromatic substrate and a higher boiling fraction comprising a mixture of monoalkylated aromatic-polyalkylated aromatic mixture;
 - f) supplying said higher boiling fraction from said separation zone to a second separation zone;
 - g) operating said second separation zone to produce a second lower boiling fraction comprising monoalkylated aromatic product and a higher boiling fraction comprising heavier polyalkylated aromatic product;
 - h) supplying at least a portion of said polyalkylated aromatic product including substantially all of the dialkylated and trialkylated aromatics in said polyalkylated product to a transalkylation reaction zone containing a molecular sieve transalkylation catalyst;
 - i) supplying said aromatic substrate to said transalkylation zone;
 - j) operating said transalkylation reaction zone under temperature and pressure conditions to maintain said aromatic substrate in the liquid phase and effective to cause disproportionation of said polyalkylated aromatic fraction to arrive at a disproportionation product having a reduced polyalkylated aromatic content and an enhanced monoalkylated aromatic content; and
 - k) supplying at least a portion of said disproportionation product to said first recited separation zone.
2. The process of claim 1 wherein said aromatic substrate comprises benzene and said alkylating agent is an ethylating or propylating agent wherein the polyalkylated aromatic content of said disproportionation product includes dialkyl and trialkyl benzenes.
3. The process of claim 2 further comprising prior to step (k) in Claim 1, supplying the output from said transalkylation zone to a third separation zone and operating said third separation zone to produce a lower boiling fraction comprising a benzene-monoalkyl benzene component and a higher boiling fraction comprising a polyalkyl benzene component and supplying said benzene-monoalkyl benzene component to said first recited separation zone in accordance with step (k) of claim 1.
4. The method of claim 3 wherein said alkylating agent is an olefin.
5. The method of claim 4 wherein said alkylating agent is ethylene.
6. In an alkylation-transalkylation process the steps comprising:
 - a) supplying a benzene feed stock into an alkylation reaction zone containing a molecular sieve aromatic alkylation catalyst;
 - b) supplying a C₂-C₄ alkylating agent to said reaction zone;
 - c) operating said reaction zone at temperature and pressure conditions causing alkylation of said benzene by said alkylating agent in the presence of said catalyst to produce an alkylated product comprising a mixture of monoalkyl and polyalkyl benzenes;

- aromatic substrate in the liquid phase and cause alkylation of said benzene by said alkylating agent in the presence of said catalyst to produce an alkylated product comprising a mixture of monoalkyl and polyalkyl benzenes;
- 5 d) recovering the effluent including benzene and said alkylated product from said primary reaction zone and supplying said alkylated product to a separation system which is operated to separately produce a benzene component, a monoalkyl benzene component and a polyalkyl benzene component;
- e) recovering a higher boiling fraction comprising said polyalkyl benzene component from said separation system
- f) supplying said higher boiling fraction to a transalkylation reaction zone containing a transalkylation catalyst selected from the group consisting of zeolite Y and zeolite omega;
- 10 g) supplying benzene to said transalkylation reaction zone;
- h) operating said transalkylating reaction zone under temperature and pressure conditions to effect liquid phase disproportionation of said polyalkyl benzene component in the presence of said transalkylation catalyst to arrive at a disproportionation product having a reduced polyalkyl benzene aromatic content and an enhanced monoalkyl benzene aromatic content; and
- i) supplying at least a portion of said disproportionation product to said separation system.
18. The method or the process of claim 17 wherein said alkylating agent is an ethylating agent or a propylating agent.
19. The method of claim 18 wherein said alkylating agent is ethylene wherein the higher boiling fraction of
- 20 step (d) of claim 17 comprises a mixture of diethylbenzene and triethylbenzene.
20. The process of claim 19 further comprising the step of prior to step (f) of claim 17 treating said higher boiling fraction to separate a polyethylbenzene fraction from a residue fraction having a boiling point higher than triethylbenzene and supplying said polyethylbenzene fraction to said transalkylation reaction zone in accordance with step (f) of claim 17.
- 25 21. In a process for the production of ethylbenzene, the steps comprising:
- a) supplying a benzene feed stock and an ethylating agent into a primary reaction zone containing an aromatic alkylation catalyst;
- b) operating said primary reaction zone under temperature and pressure conditions to effect ethylation of said benzene feed stock to produce an alkylated product comprising a mixture of ethylbenzene and polyethylbenzenes;
- 30 c) recovering said alkylated product from said reaction zone and supplying said product to a benzene separation zone;
- d) operating said benzene separation zone to produce a lower boiling fraction comprising benzene and a higher boiling fraction comprising an ethylbenzene-polyethylbenzene mixture;
- 35 e) supplying said higher boiling fraction from said benzene column to an ethylbenzene separation zone;
- f) operating said ethylbenzene separation zone to produce a second lower boiling fraction comprising ethylbenzene and a second higher boiling fraction comprising a heavy polyethylbenzene fraction;
- g) supplying said polyethylbenzene fraction from said ethylbenzene column to a transalkylation reaction zone containing a transalkylation catalyst;
- 40 h) supplying benzene to said transalkylation reaction zone;
- i) operating said transalkylation reaction zone under temperature and pressure conditions to effect disproportionation of said polyethylbenzene fraction to arrive at a disproportionation product having a reduced polyethylbenzene content and an enhanced ethylbenzene content;
- j) supplying at least a portion of said disproportionation product to a post transalkylation separation zone;
- 45 k) operating said polyethylbenzene separation zone to produce a third lower boiling fraction comprising a mixture of benzene and ethylbenzene and a third higher boiling fraction of C₉ + hydrocarbons; and
- l) recycling said third lower boiling fraction of benzene and ethylbenzene to said first recited benzene separation zone.
22. The method of claim 21 comprising splitting said disproportion product and supplying a part of said product to said polyethylbenzene separation zone in accordance with step j) and supplying another part of said product to said benzene separation zone.
- 50 23. The process of claim 21 wherein said transalkylation catalyst comprises a molecular sieve selected from the group consisting of zeolite y and zeolite omega.
24. The process of claim 23 wherein said primary reaction zone is operated under temperature and
- 55 pressure conditions to effect vapor phase ethylation of said benzene feed stock.
25. The method of claim 23 wherein said aromatic alkylation catalyst in said primary reaction zone comprises a molecular sieve selected from the group consisting of zeolite beta and zeolite omega and said primary reaction zone is operated under pressure conditions to maintain said benzene feed stock in the



European
Patent Office

EUROPEAN SEARCH
REPORT

Application Number

EP 90 87 0113

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 459 426 (INWOOD et al.) -----		C 07 C 15/02
A	DE-A-3 437 615 (G. RICHTER) -----		
A	US-A-4 555 311 (WARD) -----		
A,D	US-A-4 169 111 (WIGHT) -----		
TECHNICAL FIELDS SEARCHED (Int. Cl.5)			
C 07 C 15/00			
The present search report has been drawn up for all claims			
Place of search	Date of completion of search	Examiner	
The Hague	07 March 91	VAN GEYT J.J.A.	
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone	E: earlier patent document, but published on, or after the filing date		
Y: particularly relevant if combined with another document of the same category	D: document cited in the application		
A: technological background	L: document cited for other reasons		
O: non-written disclosure			
P: intermediate document			
T: theory or principle underlying the invention	&: member of the same patent family, corresponding document		

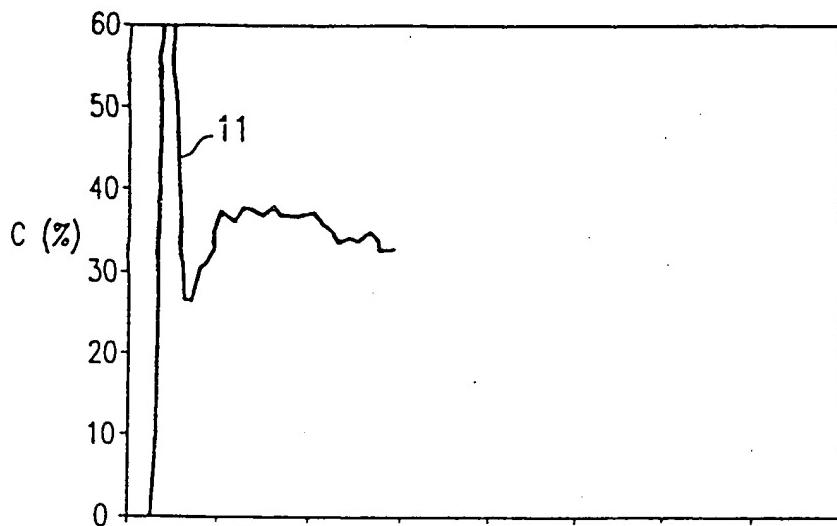


FIG. 1a

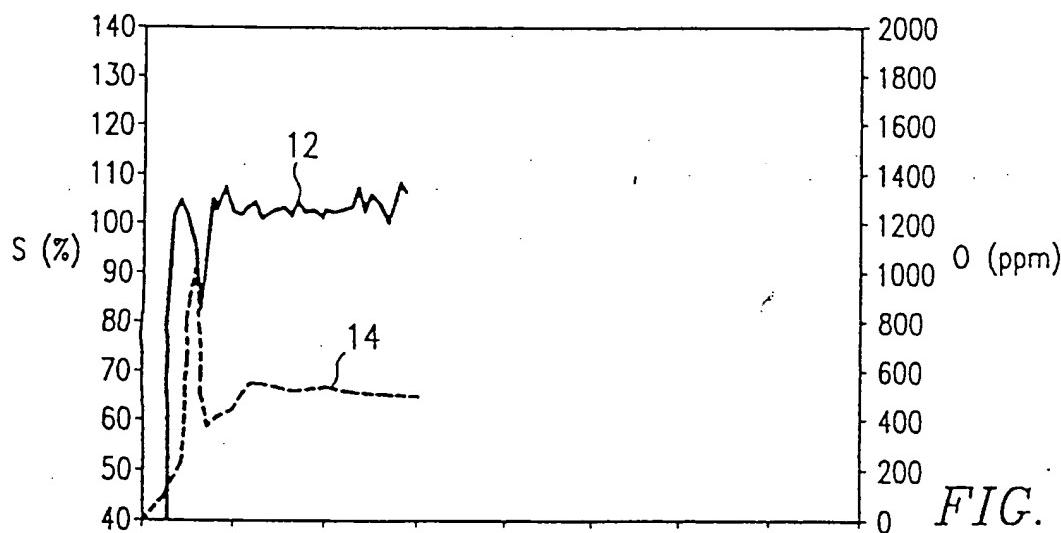


FIG. 1b

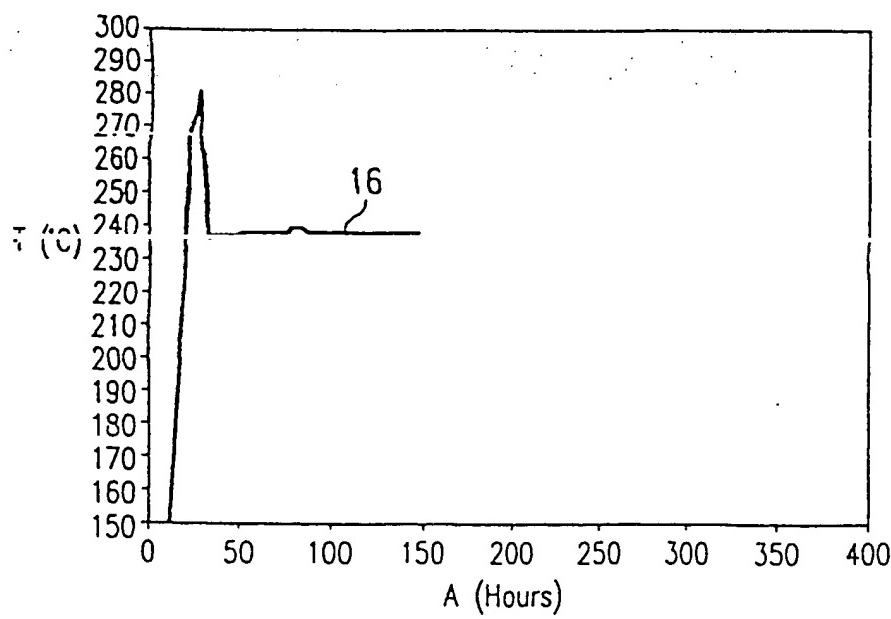


FIG. 1c

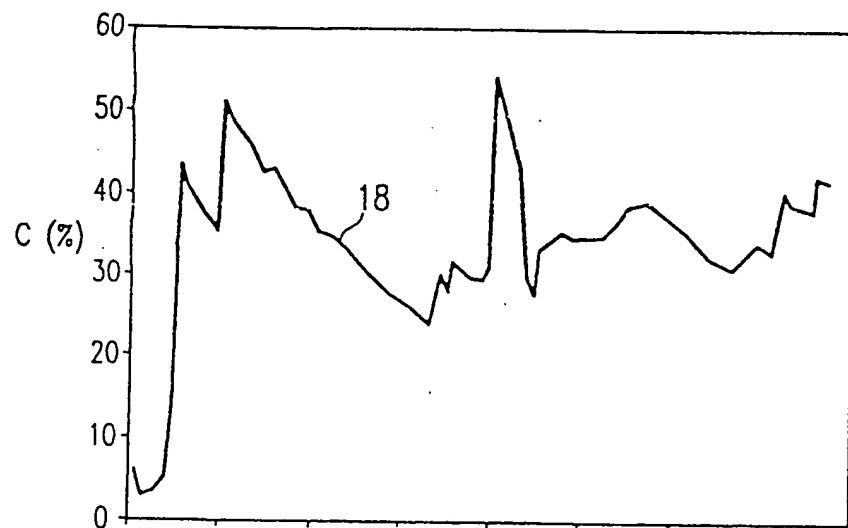


FIG. 2a

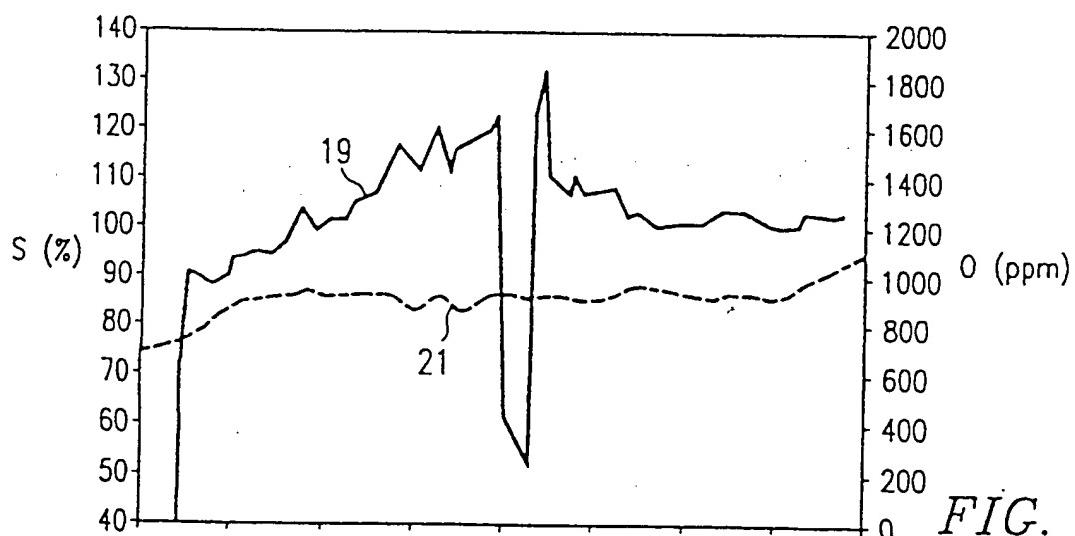


FIG. 2b

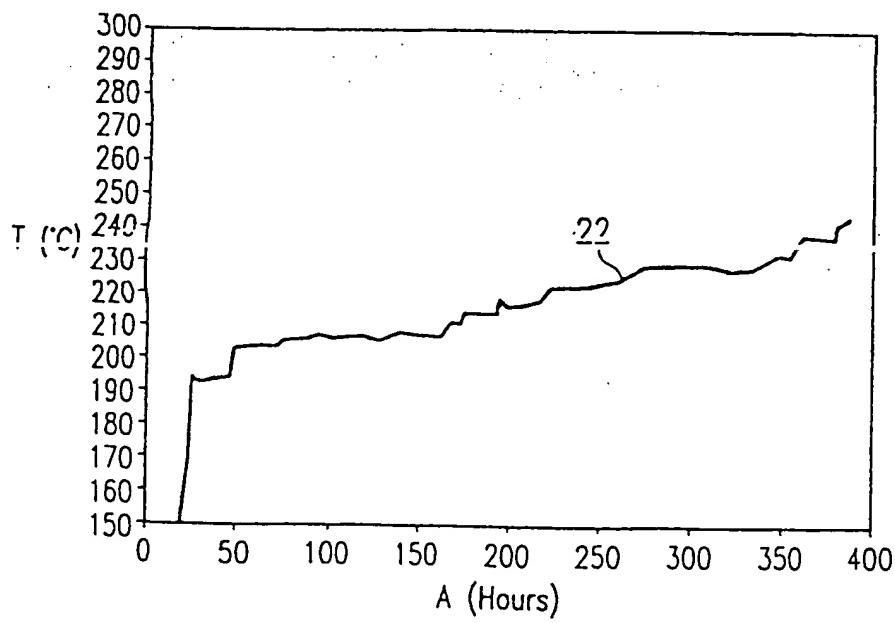


FIG. 2c

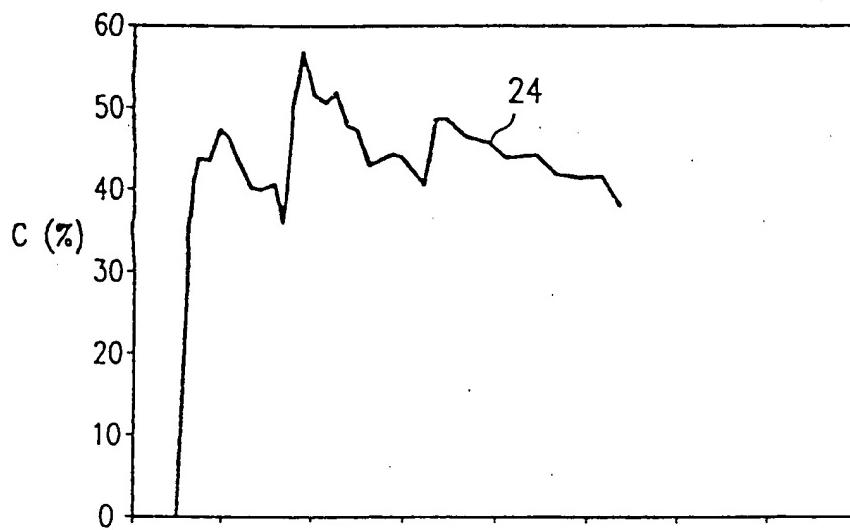


FIG. 3a

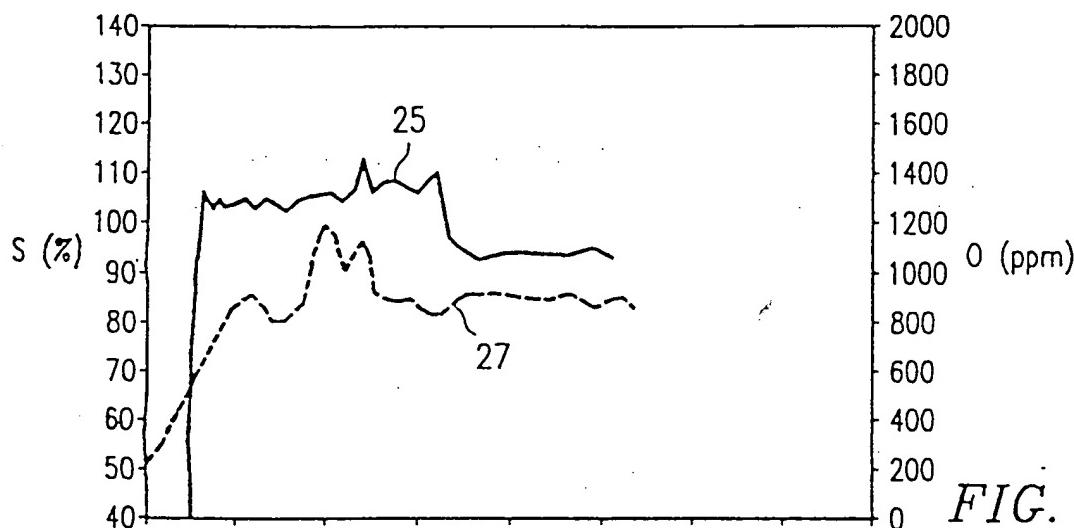


FIG. 3b

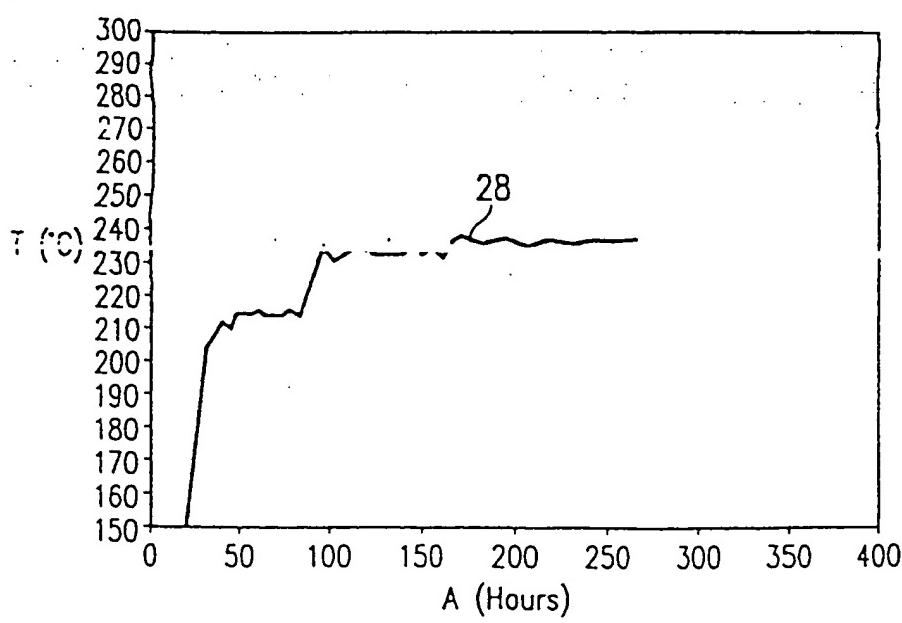


FIG. 3c

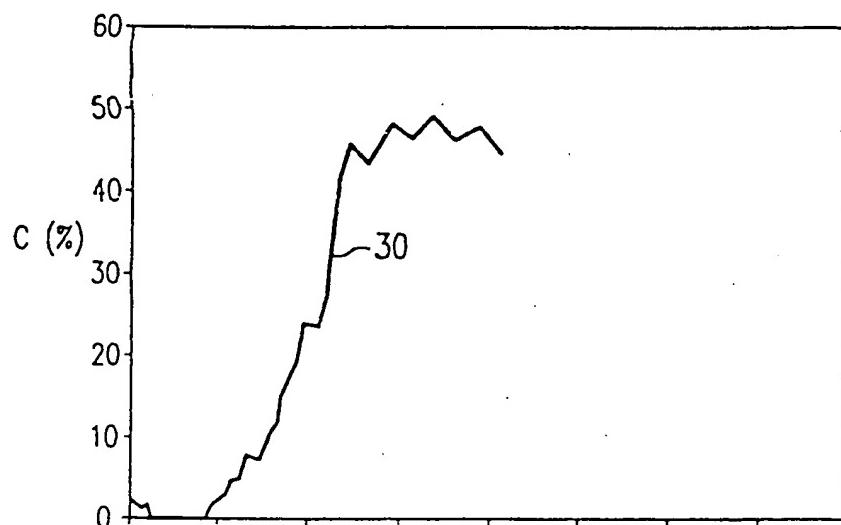


FIG. 4a

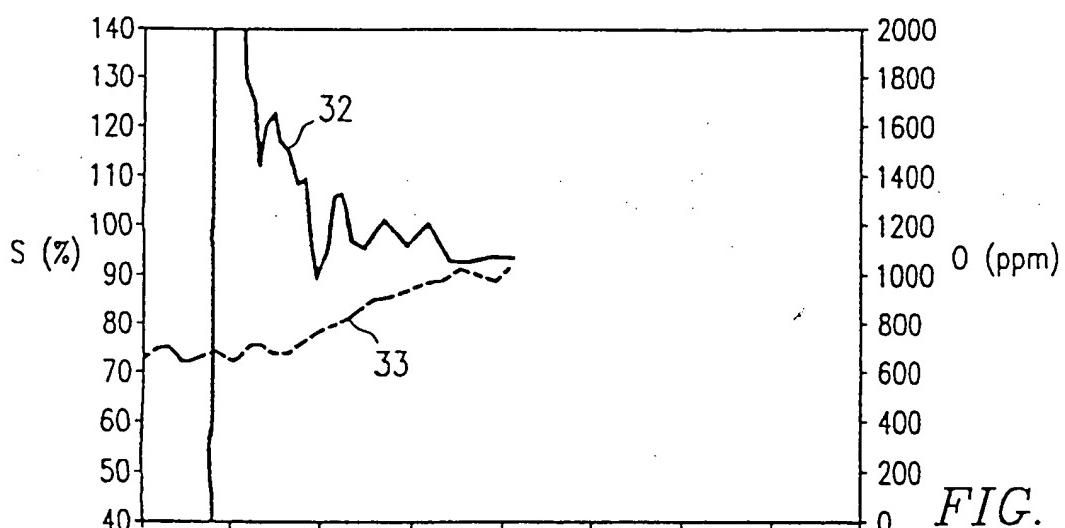


FIG. 4b

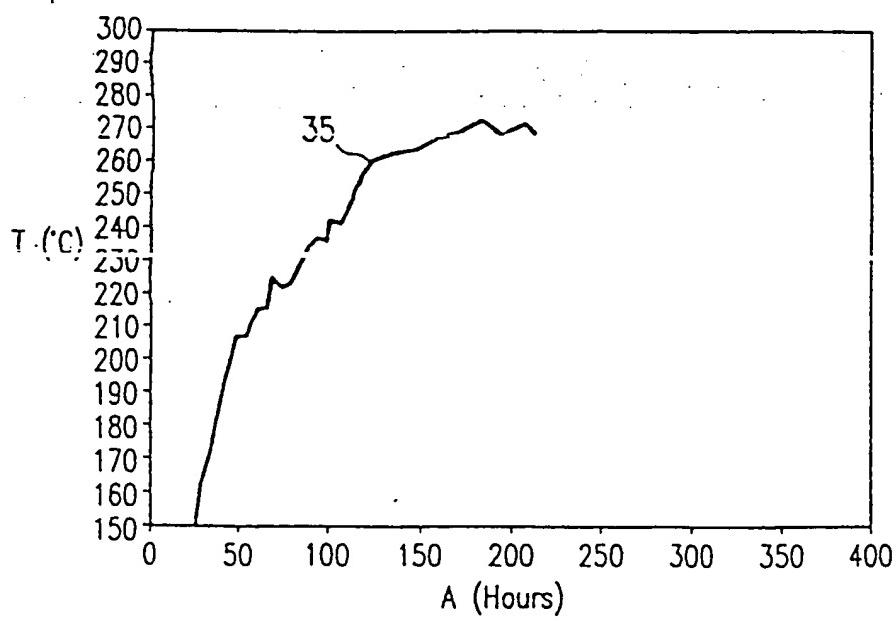


FIG. 4c

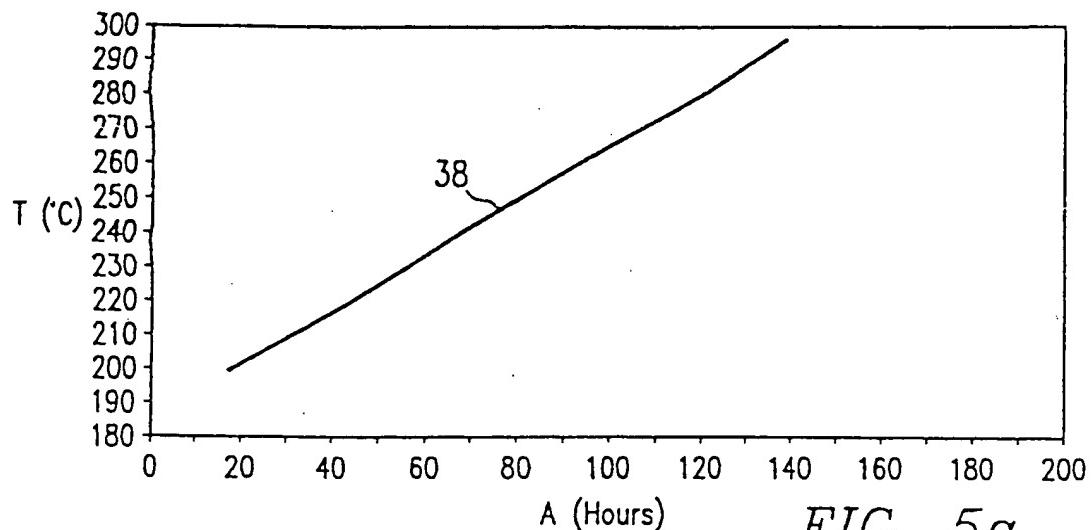


FIG. 5a

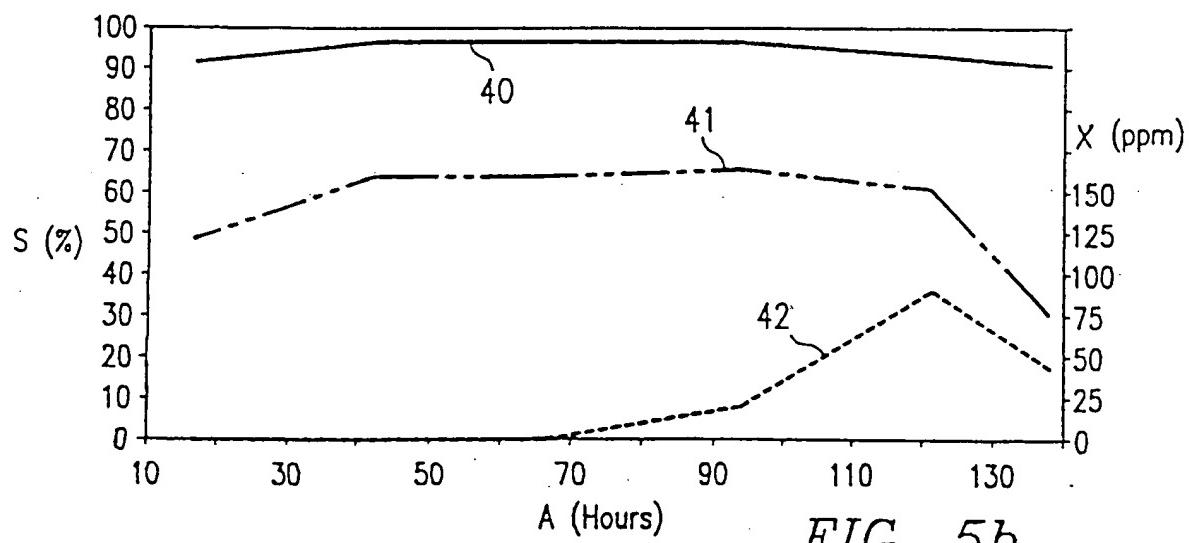


FIG. 5b

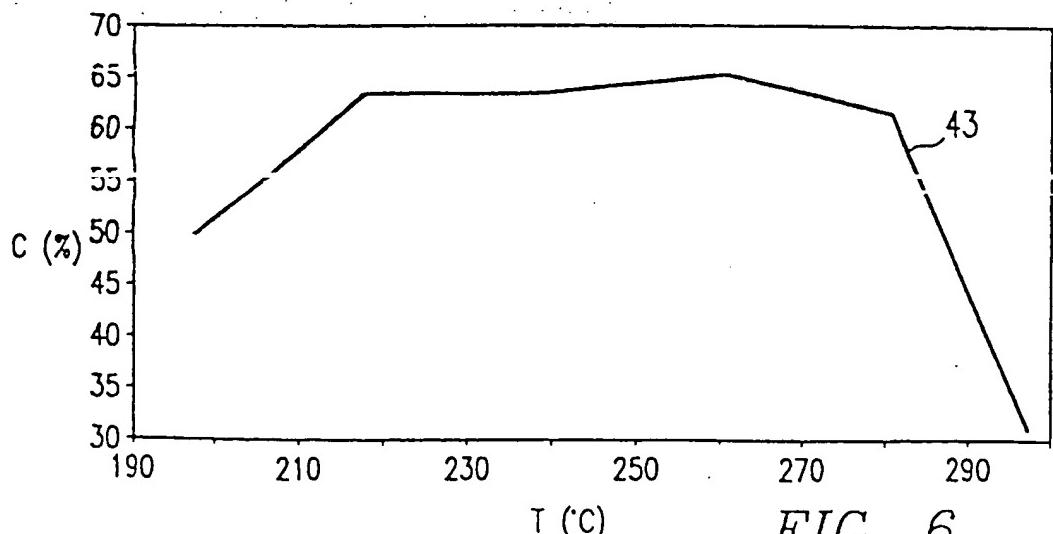


FIG. 6

FIG. 7

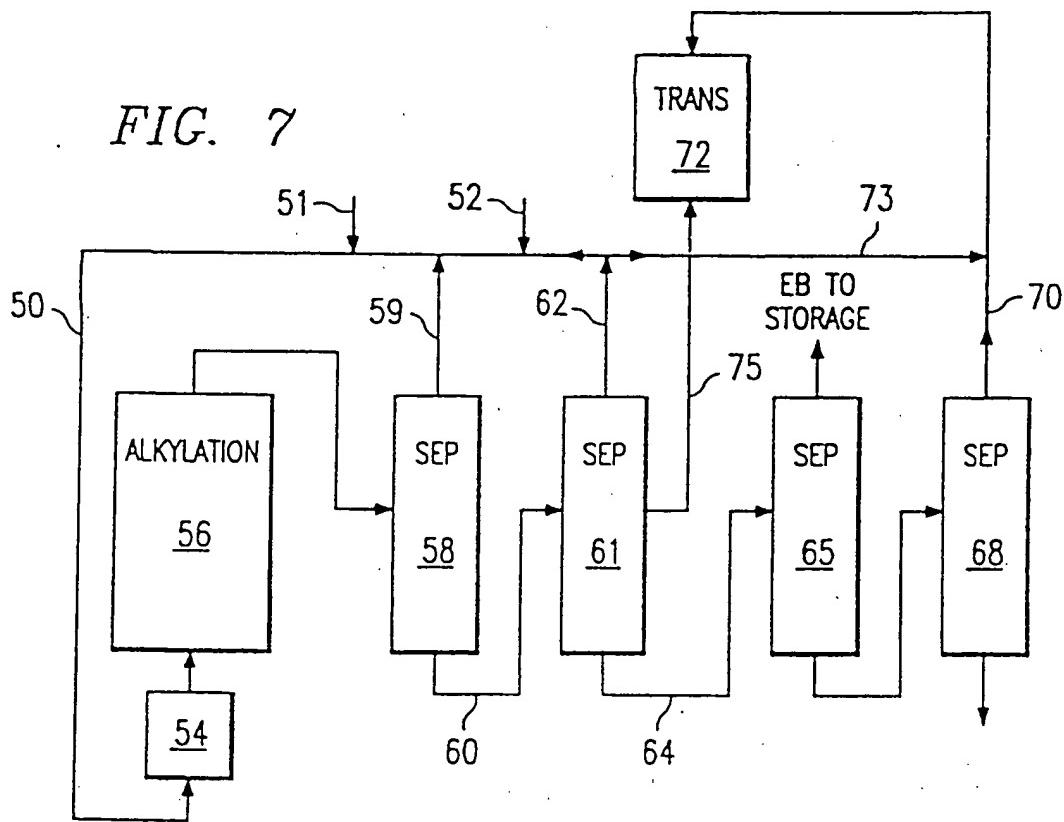


FIG. 8

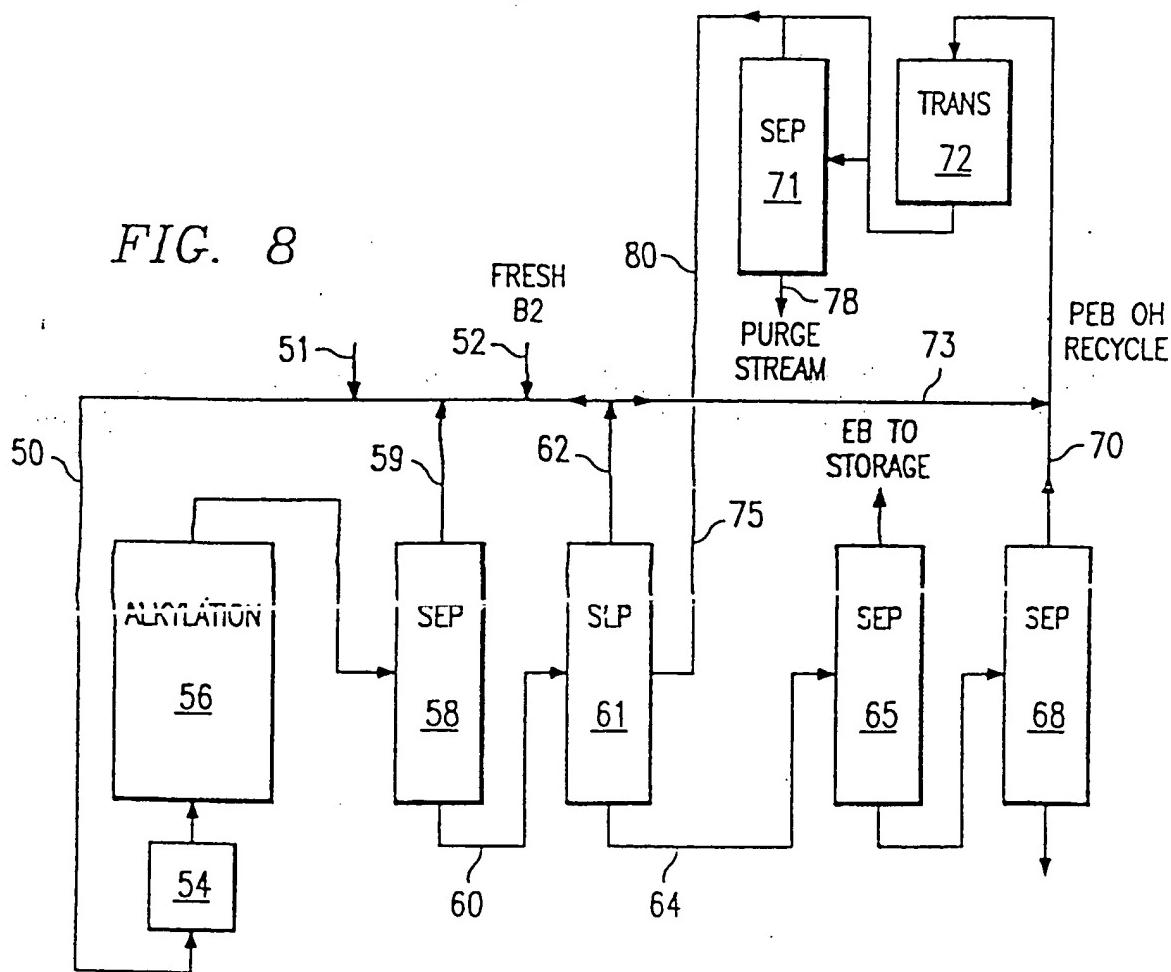


FIG. 9

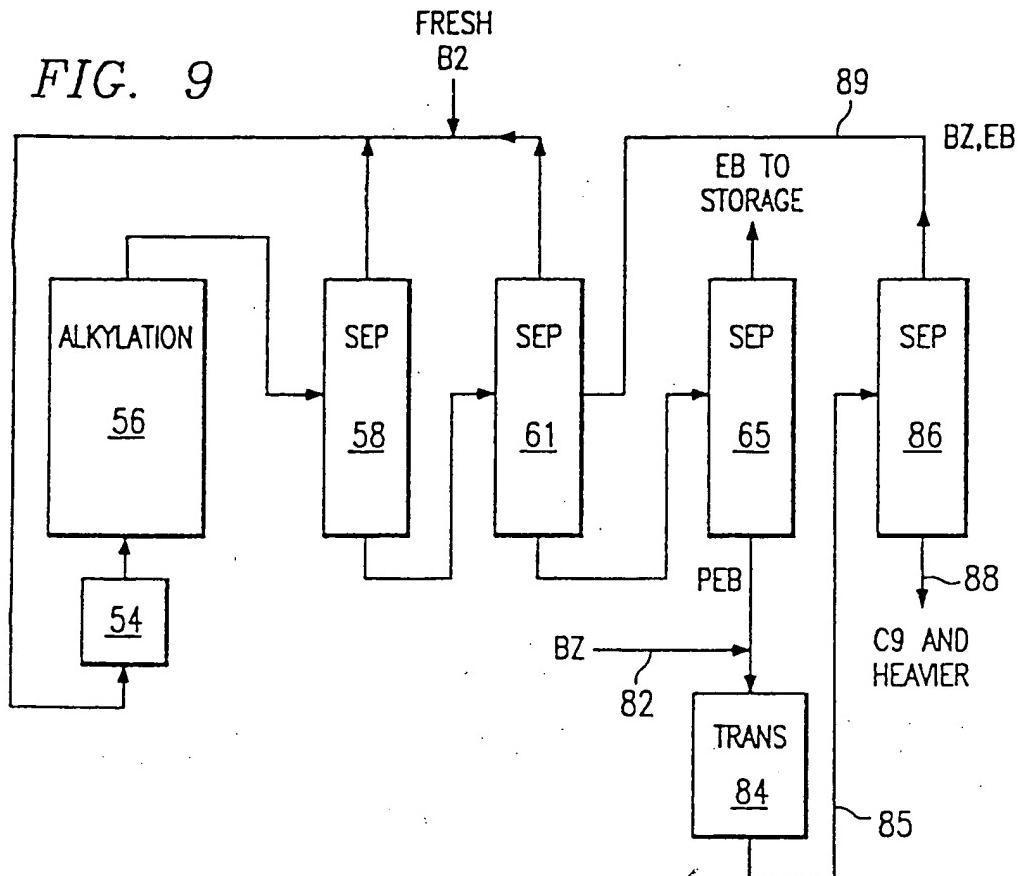


FIG. 10

